MISSOURI DEPARTMENT OF NATURAL RESOURCES
FIELD SERVICES DIVISION
ENVIRONMENTAL SERVICES PROGRAM
Standard Operating Procedures

SOP #: MDNR-ESP-213 EFFECTIVE DATE: November 14, 2005

SOP TITLE: Quality Control Procedures For Checking Water Quality Field Instruments

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SUMMARY OF REVISIONS: Minor grammatical revisions. Updated volumes for dissolved oxygen calibration. Added acceptable limit ranges for conductivity.

APPLICABILITY: The procedures outlined in this sampling protocol apply to ESP personnel who perform Quality Control audits on water quality field instruments.

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1.0 SCOPE AND APPLICABILITY

1.1 The Environmental Services Program (ESP), has a variety of portable handheld instruments (i.e., pH, conductivity and dissolved oxygen meters) and thermometers that are used by ESP field personnel for monitoring surface water, wastewater, and groundwater. Accurate, reliable and defensible field data must be obtained from these instruments and are important factors in assessing environmental conditions.

1.2 To ensure that field data are accurate and defensible, and as part of a preventative maintenance program, the instruments are checked by the ESP Water Quality Monitoring Section (WQMS) personnel (hereinafter referred to as Quality Control (QC) personnel) on a monthly basis against known standards and are documented through the described QC procedures.

1.3 This SOP refers specifically to meters and methods used at the ESP laboratory. This SOP could be used as a reference for establishing QA/QC procedures in the regional offices.

2.0 PERSONNEL QUALIFICATIONS

QC personnel shall have a working knowledge of the field equipment maintenance and calibration procedures as outlined in the manufacturers' specifications. QC personnel shall be familiar with the following standard operating procedures:

- MDNR-FSS-100 *Field Analysis of Water Samples for pH*
- MDNR-FSS-101 *Field Measurement of Water Temperature*
- MDNR-FSS-102 *Field Analysis of Specific Conductance*
- MDNR-WQMS-103 *Sample Collection and Field Analysis for Dissolved Oxygen Using a Membrane Electrode Meter*

3.0 HEALTH AND SAFETY

3.1 The calibration and certified standards are generally concentrated salt solutions prepared at various pH ranges. When handling these solutions personnel should wear protective gloves and safety glasses. Other personal protective equipment should be used as appropriate.

3.2 Mercury in thermometers is considered a hazardous material and must be properly disposed. For proper disposal of mercury-filled thermometers (broken and unbroken), the QC personnel shall contact the ESP coordinator of hazardous waste management for assistance.

3.3 Button-type batteries that contain Ag, Cd, Cr, Ni, Pb, Se, or Hg are considered hazardous materials and must be properly disposed. For disposal of button-type batteries the QC personnel shall contact the ESP coordinator

of hazardous waste management for assistance.

4.0 STANDARDS AND CERTIFIED EQUIPMENT USED

4.1 QC Certified Standard

4.1.1 The portable pH field meters are checked against a known certified standard solution that is purchased from a vendor that specializes in preparing environmental quality control standards.

4.1.2 The certified standard is accompanied with documentation stating the certification value, analytical verification and traceability summary, and expiration dates for each constituent. This documentation shall be kept on file for future reference. Both the documentation and the certified standard container shall be marked with the date that the standard was received and opened.

4.1.3 The portable conductivity field meters are checked against a standard solution that is prepared by the WQMS. However, if desired, a known certified standard solution can be purchased from a vendor that specializes in preparing environmental quality control standards. Section 4.2 provides directions on preparing conductivity standard solutions.

4.2 Preparation of Conductivity Standard Solutions

4.2.1 300 µS Range Conductivity Standard Solution

Dissolve 186.4 mg anhydrous KCl in deionized water. Dilute to 1000 mL. This prepared solution will have a conductivity of 353.25 µS at 25°C.

4.2.2 700 µS Range Conductivity Standard Solution

Dissolve 372.8 mg anhydrous KCl in deionized water. Dilute to 1000 mL. This prepared solution will have a conductivity of 706.5 µS at 25°C.

4.3 Winkler Titration for Dissolved Oxygen

The readings from the dissolved oxygen (D.O.) meters are compared against the Winkler titration method conducted by the Chemical Analysis Section (CAS) (refer to the appendix of MDNR-WQMS-103 *Sample Collection and Field Analysis for Dissolved Oxygen Using a Membrane Electrode Meter*). The CAS conducts a Winkler titration on Wednesday through Friday or an as needed basis for calibration purposes. A record of all the Winkler titration readings are documented in a bound logbook maintained by the CAS.

4.4 National Institute of Standards and Technology (NIST) Thermometer

4.4.1 The field meter's temperature sensors and individual pocket thermometer's temperature readings are compared against a NIST calibrated thermometer reading.

4.4.2 The certified mercury-filled thermometer has been calibrated at three test temperatures (0.0 °C, 37.0 °C, and 56.0 °C) or at the manufacturers' specifications. The thermometer is supplied with documentation to prove its traceability to the NIST. Refer to the 21st edition of *Standard Methods for the Examination of Water and Wastewater,* section 2550 for further information regarding thermometer specifications.

5.0 FIELD INSTRUMENT CHECK-OUT PROCEDURES

5.1 As part of quality control and instrument tracking purposes, field instruments must be checked out by field personnel prior to field use. The following information shall be recorded on the equipment sign-out sheet: meter type and property number, date meter was checked out and returned, and the user's name. Upon return from the field, field personnel shall record any problems/comments regarding the meter used in the comment section of the sign-out sheet.

5.2 Once a meter returns from the field, QC personnel shall conduct the following check-in procedures: check the meter and probe for damage, replace all calibration buffer solutions with fresh solutions, and clean the meter and case. The individual who conducts the meter check-in must initial and date the sign-out sheet in the date-checked column.

5.3 The necessary corrective steps should be taken if the user noted any problems on the equipment sign-out sheet and before the instrument is placed back into service. QC personnel should confer with the user and the necessary ESP Standard Operating Procedures regarding the problems encountered. Any corrective steps shall be noted in the appropriate QC field instrument logbook (see section 6.0).

6.0 QC FIELD INSTRUMENT LOGBOOKS AND LOG SHEETS

6.1 All QC procedures and any preventative/corrective maintenance performed on the field meters by QC personnel shall be recorded in a dedicated bound logbook for each instrument type (pH, conductivity, D.O., and thermometer). The logbooks shall, at a minimum, contain the following information:

- the date the QC procedure or any preventative maintenance was performed,
- the initials of the person performing the procedure,
- the lot number, certified value, and performance acceptance limits of the certified standard used,

- any comments regarding the field instruments (e.g., sluggish response, calibration problems, parts replaced, etc.).

6.2 Log sheets for each month shall be kept in a labeled three-ring binder. The log sheets provide consistency and uniformity in monthly QC checks. They contain detailed information pertaining to all field meters. If an instrument is unavailable (in the field, being serviced, etc.) at QC time, it shall be recorded as such. The log sheets shall contain the following information:

- the lot number, certified value, and performance acceptance limits of the certified standard used,
- type of instrument, model number and property number of all instruments available for field use,
- the certified standard or conductivity standard readings from the field instrument,
- the temperature readings while in the certified standard or conductivity standard,
- the NIST calibrated thermometer reading of the certified standard or conductivity standard.

6.3 The logbooks and log sheets will be maintained by the WQMS.

7.0 QC PROCEDURES FOR THE pH METERS

7.1 The QC personnel shall inspect each meter and its components. The pH meters and probes shall be cleaned and checked for fouling and breakage. If damage has occurred, then the meter and components shall be repaired or replaced prior to conducting the rest of the QC procedure (refer to MDNR-FSS-100 *Field Analysis of Water Samples for pH*).

7.2 The QC personnel shall ensure that each meter has a stock of two 9-volt batteries located in the meter case for back-up.

7.3 As part of the monthly QC check of all WQMS meters, the calibration pH buffer solutions (4.0, 7.0, and 10.0) stored within the meter case shall be discarded and replaced with fresh buffer solutions. Buffer solutions for other field meters should be discarded and replaced as they are returned from field use (See section 5.2).

7.4 Prior to calibration and according to the manufacturers' specifications, the meter shall be checked for proper operation through the power-up and self-test procedures as outlined in the meter's instruction manual. If any problems are found during the self-test, the instruction manual shall be referred to for further operational assistance. If necessary, the meter will be returned to the manufacturer for repairs. If the pH meter is working properly, then proceed with the meter's calibration procedures. Refer to MDNR-FSS-100 *Field Analysis of Water Samples for pH* for calibration

procedures.

7.5 Immediately following the calibration process many of the pH meters will display the percent efficiency value, also referred to as the percent slope. The QC personnel shall record the percent slope value in the logbook. The percent slope should read 100%. If the value is off by more than ± 5 %, then this is an indication that the pH probe is fouled and needs to be rejuvenated (refer to the appendix of MDNR-FSS-100 for the pH probe rejuvenation process) or replaced prior to being returned to service.

7.6 A portion of the certified standard solution shall be poured into a clean glass beaker. Place the pH meter's electrode and automatic temperature compensation (ATC) probe into the standard and agitate slightly until a stable reading is displayed. The meter's pH and temperature readings shall be recorded in the pH meter logbook. The NIST calibrated thermometer shall be placed into the standard solution. When the reading stabilizes, record the temperature in the logbook.

7.6.1 If the pH meter reads outside of the certified standard's acceptable limit range (± 0.2 standard units), then the meter and probe should be inspected. If the meter checked out during the self-test, then the probe is fouled or a bad probe connection may have occurred.

7.6.2 If the probe connection is secure, the QC personnel can assume the probe is fouled and malfunctioning. To ensure the probe is the cause of the erratic readings, attach a functioning pH probe to the meter. The malfunctioning probe should be rejuvenated. If the probe rejuvenation process still fails to give acceptable readings, then the probe should be discarded and replaced.

7.6.3 If the erratic readings were caused due to a loose or bad connection, the connection should be tightened and cleaned of debris. If a good connection cannot be obtained, the probe should be replaced.

7.6.4 If the pH meter's ATC probe reading is off by more than ± 1.0 °C of the NIST calibrated thermometer (or the manufacturer's stated accuracy for temperature), then the ATC probe should be replaced.

8.0 QC PROCEDURES FOR THE CONDUCTIVITY METERS

8.1 Preparation of Calibration Standard Solution for Orion Model 125 Meters:

A fresh aliquot of 1413 microSiemens per centimeter (µS/cm) calibration standard should be prepared, at a minimum, on a monthly basis. The calibration standard is prepared by diluting 0.7456 grams of anhydrous potassium chloride (KCl) in one liter of deionized water (refer to MDNR-FSS-102 *Field Analysis of Specific Conductance*).

8.2 The conductivity meters and probes shall be cleaned and checked for fouling and breakage. If damage has occurred, then the meter and components shall be cleaned, repaired, or replaced prior to conducting the QC procedure (refer to MDNR-FSS-102 *Field Analysis of Specific Conductance*).

8.3 The QC personnel shall ensure that each meter has a stock of two 9-volt batteries located in the meter case for back-up.

8.4 Prior to the monthly QC check, the calibration standard solutions stored within the meter case shall be discarded and replaced with fresh calibration solutions.

8.5 Prior to calibration, and according to the manufacturer's specifications, the conductivity meter shall be checked for proper operation through the power-up and self-diagnostics checkout procedures (refer to the meter's instruction manual or MDNR-FSS-102 *Field Analysis of Specific Conductance*). If any problems are found during the self-test, refer to the instruction manual for further operational assistance and, if necessary, return the meter to the manufacturer for repairs. If the conductivity meter is working properly, then proceed with the meter's calibration procedures. Refer to MDNR-FSS-102 *Field Analysis of Specific Conductance* for calibration procedures.

8.6 Immediately following the calibration process, many of the meters will momentarily display the recalculated cell constant value then return to the measurement mode. QC personnel shall record the recalculated cell constant in the logbook.

8.7 While the meter is in the measurement mode and the probe is still in the calibration standard, QC personnel shall also record the adjusted conductivity value (referred to as the default value). The default value is the calibration standard's new value at the current temperature and at the readjusted cell constant.

8.8 Pour a portion of the conductivity standard solution (300 µS range and 700 µS range) into a clean glass beaker. Place the conductivity probe into the standard and agitate slightly until a stable reading is displayed. Record the conductivity and temperature readings in the conductivity logbook. Place the NIST calibrated thermometer into the standard solution, wait for a stable reading, and record its' temperature in the logbook.

8.8.1 If the conductivity meter reading is outside of the certified standards acceptable limit range of ± 10 % or off by more than ± 1.0 °C (or the manufacturer's stated accuracy for temperature) of the NIST calibrated thermometer's reading, then the meter and probe must be inspected. If the meter works properly during the self-test, then the probe is fouled or a bad probe connection may have occurred.

8.8.2 If the probe connection is secure, the QC personnel can assume the probe is fouled and malfunctioning. To ensure the probe is the cause of the erratic readings, attach a functioning conductivity probe to the meter. The malfunctioning probe should be replaced if cleaning the probe does not correct the problem.

8.8.3 If the erratic readings were caused by a loose or bad connection, the connection should be tightened and cleaned of debris. If a good connection cannot be obtained, the probe should be replaced.

9.0 QC PROCEDURES FOR THE DISSOLVED OXYGEN METERS

9.1 As explained in section 4.3, the CAS conducts a Winkler titration on Wednesday through Friday or an as needed basis for calibration purposes. An aliquot of water (approximately 500 mL in an Erlenmeyer flask) shall be obtained from the CAS along with the Winkler titration recording for the day. For comparable D.O. readings, it is best to obtain water from the CAS immediately after the Winkler titration has been conducted.

9.2 To obtain an accurate D.O. reading, the container of water should be placed on a stir plate and lightly stirred with a stir bar throughout the QC procedure. In addition, to prevent increasing the temperature of the water sample, insulated material should be placed between the Erlenmeyer flask and the stir plate.

9.3 The D.O. meter and probes should be cleaned and checked for fouling and breakage. The D.O. probe membrane should be checked for air bubbles, discoloration, and algal growth across the membrane.

9.3.1 If air bubbles have formed under the membrane or if any discoloration of the membrane has occurred, the membrane should be removed, fill solution (KCl) replaced, and a new membrane installed (refer to the meter's operating instruction manual or MDNR-WQMS-103 *Sample Collection and Field Analysis for Dissolved Oxygen Using a Membrane Electrode Meter*).

9.3.2 Algal growth can be carefully wiped away by using a dampened soft cloth or Kimwipe.

9.4 Prior to calibration, the D.O. meter should be allowed to warm up and the probe allowed to stabilize to the ambient air temperature for at least 20-30 minutes or until the temperature readings stabilize. Air temperature differences between the NIST calibrated thermometer and the individual meters may vary depending upon 1) the length of time the probe is allowed to stabilize and 2) the temperature of the water used to moisten the sponge within the calibration cup. This is why it is important to allow adequate time

for the meters to warm up.

9.5 Once the air temperature readings have stabilized, the QC personnel shall record the D.O. meter's air temperature readings in the D.O. logbook.

9.6 To determine the accuracy of the D.O. meters against the Winkler titration value, the meters should be calibrated at the same air temperature. Follow the air calibration procedures as described in MDNR-WQMS-103 *Sample Collection and Field Analysis for Dissolved Oxygen Using a Membrane Electrode Meter* to calibrate the D.O. meters.

9.6.1 If the meter's temperatures vary more than ± 1.0 °C from one another and the NIST calibrated thermometer, allow the probes to stabilize a few minutes longer before recording the air temperatures in the D.O. log book.

9.6.2 If a meter's temperatures read more than ± 1.0 °C of the NIST calibrated thermometer's air and solution temperatures then the D.O. probe should be replaced.

9.7 Submerge approximately half of the D.O. probe in the water and agitate slightly to remove any air bubbles. Gently stir the probe in a circular motion until the D.O. reading stabilizes. Record the dissolved oxygen concentration and temperature readings in the D.O. logbook. To ensure the temperature is stable through the QC procedure, the temperature should be checked at the beginning and at the end of the procedure.

9.8 If the D.O. reading is off by ± 0.5 mg/L of the Winkler titration reading, conduct one or more of the following procedures to determine the source of erratic readings. After each procedure the meter readings should be checked again. Refer to the instrument's instruction manual for further operational assistance if the following procedures fail to obtain a D.O. reading within the stated range:

- Make sure all cable and probe connections are tight;
- Replace the probe's oxygen sensor membrane, refill with fresh KCl fill solution, and recalibrate the meter;
- Place an operational probe body on the existing D.O. cable and recalibrate the meter. If the reading is within ± 0.5 mg/L of the Winkler titration, then the malfunctioning probe body needs to be replaced. If the reading is still off by ± 0.5 mg/L then;
- Place an operational cable on the existing D.O. probe. If the reading is still off by ± 0.5 mg/L of the Winkler titration, then the D.O. cable needs to be replaced.

9.9 If the D.O. meter's temperature reading is off more than ± 1.0 °C (or the manufacturer's stated accuracy for temperature) of the NIST calibrated

thermometer, then the probe should be replaced.

10.0 QC PROCEDURES FOR THE POCKET THERMOMETERS

10.1 Pocket thermometers will be checked monthly at various temperatures (high to low ranges) within a controlled environment (e.g., environmental chamber) or exposed to atmospheric conditions. The selected temperatures should resemble or bracket various ambient seasonal temperatures.

10.2 The QC personnel shall check the thermometers for damage and ensure the thermometer's column does not contain a separation.

- The pocket thermometer shall be properly discarded and replaced if damage to the thermometer has occurred.
- Swing the thermometer (bulb down) in an arc several times to remove any separations in the column. Refer to the heating or cooling methods stated in MDNR-FSS-101 *Field Measurement of Water Temperature* if the separation remains.

10.3 The pocket thermometers and the NIST calibrated thermometer should be placed in a beaker filled with one liter of water and allowed to stabilize at the desired temperature for approximately one hour to obtain stable readings. Once the desired temperature has been reached, the pocket thermometer's temperature readings will be compared to the NIST calibrated thermometer reading and recorded in the thermometer logbook.

10.4 To ensure that accurate temperatures are obtained, the thermometers should remain in the beaker of water when recording the temperature readings. After a thermometer's temperature reading has been recorded in the logbook, it may be removed from the beaker of water.

10.5 If the pocket thermometer's temperature reading is off by more than ± 1.0 °C (or the manufacturer's stated accuracy for temperature) of the NIST calibrated thermometer, then the pocket thermometer should be properly discarded and replaced (see section 3.2).

11.0 QC PROCEDURES FOR THE POCKET PENS

11.1 Due to their short life span (approximately one year) the pH and conductivity pens' performances are not tracked in the database (see section 12.0). However, the pens are identified using a numeric code. The code consists of the date/month/year (00/00/00) the pens were received followed by a sequential number for multiple pens received on the same date. For example, a group of three pH pens received on October 6, 2001, would be coded 100601-1, 100601-2, and 100601-3.

11.2 QC personnel shall ensure that each pen is clean and has a stock of at least

six button-type batteries for back-up (See section 3.3).

11.3 Prior to the QC check, the calibration standard solutions stored within each pen case shall be discarded and replaced with fresh buffer solutions.

11.4 The pens shall be calibrated according to the manufacturer's instructions.

11.5 Pour a portion of the certified standard or conductivity solution into a clean glass beaker. Place the pen into the standard and agitate slightly until a stable reading is displayed. Then record the pen's identification code and the readings in the appropriate logbook.

11.6 When a pen is no longer able to calibrate or measure within the standards acceptable range, the pen should be discarded and replaced prior to the next monthly QC check. The QC personnel shall record in the appropriate logbook that the pens were checked and that all malfunctioning pens were discarded.

12.0 DATA ENTRY OF QC RESULTS

Immediately upon completing the monthly QC procedures, the QC results shall be entered into a database for further analysis and tracking purposes. Information regarding the meter's property number, the meter's/instrument's readings, the certified/true value, and the data entry person's initials shall be entered in the database. Upon completing data entry for each meter/instrument type, the data entry person shall initial and date the QC field instrument logbooks.

13.0 REFERENCES

MDNR-FSS-100 *Field Analysis of Water Samples for pH.*

MDNR-FSS-101 *Field Measurement of Water Temperature.*

MDNR-FSS-102 *Field Analysis of Specific Conductance.*

MDNR-WQMS-103 *Sample Collection and Field Analysis for Dissolved Oxygen Using a Membrane Electrode Meter.*

Orion Laboratory Products Group Model 125 and 150 Conductivity Meters Instruction Manual.

Orion Laboratory Products Group Portable pH/ISE Meters Instruction Manual for Model 230A, Model 250A, Model 290A.

Standard Methods for the Examination of Water and Wastewater, 2005, 21st Edition.

Yellow Springs Instruments (YSI) Co., Inc. Instruction Manuals for YSI Models 54, 57, and 58.